



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 376 674
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 89313583.0

(51) Int. Cl.⁵ C08G 18/10, C08G 18/50,
B05D 1/02

(22) Date of filing: 27.12.89

(30) Priority: 28.12.88 JP 328944/88

(43) Date of publication of application:
04.07.90 Bulletin 90/27

(84) Designated Contracting States:
DE FR GB IT NL

(71) Applicant: MITSUI TOATSU CHEMICALS INC.
No. 2-5, Kasumigaseki 3-chome
Chiyoda-Ku Tokyo 100(JP)

(72) Inventor: Taniguchi, Kazuo
4-5-45 Dai Kamakura-Shi
Kanagawa-Ken, 247(JP)
Inventor: Ogura, Tetsuyoshi
4-10-8 Hisagi
Zushi-Shi Kanagawa-Ken, 249(JP)
Inventor: Imaoka, Kazuhiro
3-5 Shiomidai Isogo-Ku
Yokohama-Shi Kanagawa-Ken, 235(JP)
Inventor: Sakaguchi, Hiroaki
1071-2, Nakano-Cho Sakae-Ku
Yokohama-Shi Kanagawa-Ken, 247(JP)

(74) Representative: Hayward, Denis Edward Peter
et al
Lloyd Wise, Tregear & Co. Norman House
105-109 Strand
London WC2R 0AE(GB)

(54) Spray urethane elastomer.

(57) This invention relates to a process for manufacturing a spray urethane elastomer, more particularly to a process for manufacturing a solventless, non-cellular spray urethane elastomer, which comprises spraying a partial prepolymer component having a high molar ratio of NCO/OH prepared from an organic polyisocyanate and from polytetramethylene ether glycol (PTMEG) having a molecular weight of 400 to 2000 and a resin component containing the PTMEG, a specified chain extender and an organobismuth compound catalyst onto a substrate by use of a two components high pressure spray machine.

According to the present invention, spraying only of the stock solutions by use of the two components high pressure spray machine accomplishes coating and the stock solutions are cured in one second to ten and several seconds after being sprayed without producing cells even when thick-coated. Therefore, the present invention makes it possible to effect wet-on-wet coating within a short period of time, resulting in making it possible to accomplish a coating having a predetermined thickness in a short period of time.

An elastomer, which has been coated, is excellent at modulus, tensile strength, elongation, tear strength, heat resistance, and the like, such as pipe, tank and the like, waterproof materials such as concrete for the roof and outside wall which need waterproofness, thick-coated protective coating for a thermal insulant such as rigid polyurethane foam, polystyrene foam, board or the like, seamless floor covering material, open mold molding by use of a mold made of metal or resin, and the like.

EP 0 376 674 A1

Spray Urethane Elastomer

The present invention relates to a process for manufacturing a spray urethane elastomer, and more particularly to a process for manufacturing a solventless spray urethane elastomer prepared from a prepolymer component obtained by a specific formulation and a resin component by use of two components high pressure spray machine.

5 The conventional manufacturing processes of spray urethane elastomer include, for example, a solvent dilution process (in Adiprene Bulletin by Du Pont de Nemours) which process comprises dissolving a prepolymer having a terminal isocyanato group and a highly active aromatic amine curing agent such as diphenylmethanediamine and the like in a solvent separately and coating by use of the conventional two components spray machine (pressure : about 70Kg/cm²; a process which comprises diluting in a solvent
 10 and mixing the above prepolymer and a low active aromatic amine curing agent such as 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) and the like, followed by spraying within a pot life by use of a high pressure one component spray machine (see Japanese Patent Application Laid-Open No. 17430/74 by MITSUI TOATSU CHEMICALS, INC.) ; a process using a high boiling solvent to remain it in a coated product ; a process comprising reacting a partial prepolymer with a mixture of a high molecular weight
 15 polyol and a low molecular weight polyol (see Japanese Patent Application Laid-Open Nos. 134077/75 and 147329/75 by MITSUI TOATSU CHEMICALS, INC.) ; and the like.

The above process by use of the solvent raises environmental pollution problems due to the solvent, the thermal energy loss problems due to forced heat curing in the case of thick-coating, and problems of developing a large amount of foam from the coated product in the case of thick-spraying at one time
 20 because of needing to evaporate the solvent from the coated product. The process which uses the high boiling solvent to prevent foams from developing and allows the solvent to remain in the coated product, raises such problems that the solvent is lost when the coated product is used over a long period of time due to migration, evaporation, elution into rainwater and the like, resulting in deterioration of the coating taking place along with cracking, shrinkage, etc.

25 A process, in which coating is carried out thinly and repeatedly, has such a drawback that it takes a long period of time to accomplish the coating.

A process, in which, for example, a carbodiimide modified liquid diphenylmethane diisocyanate (hereinafter diphenylmethane diisocyanate is referred to as MDI.) or a partial prepolymer of MDI is reacted with a mixture of a high molecular weight polyol and a low molecular weight polyol to prepare a coated
 30 product, has such a drawback that the low molecular weight polyol so highly hydroscopic as to result in a competitive reaction between the hydroxyl group and moisture, in being easily foamed, in developing pinholes, craters and the like on the coated product, and in reducing the specific gravity and strength of the coated product.

The above processes all have such drawbacks as reduction in density of the coated product, and consequently as deterioration in physical properties, deterioration in surface properties, etc., because foaming due to moisture in the air and foaming due to moisture caused by hydroscopicity of the polyol component, etc. are not completely controlled.

35 The conventional processes for manufacturing urethane elastomer include such ones as cast molding, millable polyurethane process, thermoplastic molding, etc. It was very difficult for the above processes to apply to a lining in order to impart abrasion resistance, etc. to a surface having a complicated configuration.

This invention relates to a process for manufacturing a spray urethane elastomer, more particularly to a process for manufacturing a solventless, non-cellular spray urethane elastomer, which comprises spraying a partial prepolymer component having a high molar ratio of NCO/OH prepared from an organic polyisocyanate and from polytetramethylene ether glycol (PTMEG) having a molecular weight of 400 to
 40 2000 and a resin component containing the PTMEG, a specified chain extender and an organobismuth compound catalyst onto a substrate by use of a two components high pressure spray machine.

45 According to the present invention, spraying only of the stock solutions by use of the two components high pressure spray machine accomplishes coating and the stock solutions are cured in one second to ten and several seconds after being sprayed without producing cells even when thick-coated. Therefore, the present invention makes it possible to effect wet-on-wet coating within a short period of time, resulting in making it possible to accomplish a coating having a predetermined thickness in a short period of time.

An elastomer, which has been coated, is excellent at modulus, tensile strength, elongation, tear strength, heat resistance, and the like, such as pipe, tank and the like, waterproof materials such as concrete for the roof and outside wall which need waterproofness, thick-coated protective coating for a thermal insulant such as rigid polyurethane foam, polystyrene foam, board or the like, seamless floor

covering material, open mold molding by use of a mold made of metal or resin, and the like.

The present inventors intensively studied on a process for manufacturing a spray urethane elastomer which is capable of being thick-coated and is free of the influence of moisture, resulting in accomplishing the present invention by selecting a specified catalyst.

- 5 The molding process by spraying in the present invention makes possible moldings and applications which have been considered impossible.

The process of the present invention is capable of being applicable to a vertical surface because of a high initial curing speed, completely preventing cracks from developing by preventing cheese-like jel-

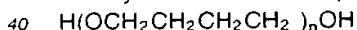
- 10 lification which initially takes place, and obtaining a molded product having satisfactory physical properties. That is, a specifically excellent starting material system has been found, comprising a combination of a polytetramethylene ether glycol based polyether, a highly active aromatic polyamine and an organobismuth catalyst capable of providing an elastomer having excellent physical properties, particularly high abrasion resistance.

15 The reaction rate of the starting material system in the present invention is so high that the conventional stirring machine is unusable and a special spray machine is needed. It is an essential requirement that a two components high pressure spray machine is used, that respective hydraulic pressures are raised up to about 100 Kg/cm², followed by mixing with a colliding and mixing gun, and immediately followed by spraying. The present invention is accomplished by subjecting the above system to molding by use of the above spray machine.

- 20 That is, the present invention provides a process for manufacturing a solventless spray urethane elastomer which comprises spraying directly onto a substrate by use of a two components high pressure spray machine, in a NCO/OH molar ratio of about 0.9 to 1.3 of undermentioned (a) and (b) components, (a) a partial prepolymer component prepared by reacting an organic polyisocyanate and a polytetramethylene ether glycol having a molecular weight of 400 to 2,000 at a NCO/OH molar ratio of 5 to 40, and (b) a resin component prepared by mixing a polytetramethylene ether glycol, having a molecular weight of 400 to about 2000, an active aromatic polyamine as a chain extender and free of an electron attractive group on the aromatic nucleus and an organobismuth compound as a catalyst by use of a two components high pressure spray machine.

25 Examples of the organic polyisocyanate used in the present invention include 2,4-tolylene diisocyanate (hereinafter referred to as 2,4-TDI), 2,6-TDI and a mixture of 2,4-TDI and 2,6-TDI, 2,4'-MDI, 4,4'-MDI and a mixture of 2,4'-MDI and 4,4'-MDI, xylene diisocyanate (XDI), 2,4-and/or 4,4-dicyclohexylmethane diisocyanate (hydrogenated MDI), isophorone diisocyanate (IPDI), hexamethylene diisocyanate (HDI), hydrogenated xylene diisocyanate (HXDI), crude TDI, polymethylene polyphenyl polyisocyanate (crude MDI, polymeric MDI), isocyanurate-modified ones, carbodiimide modified ones, biuret modified ones and urethaneimine modified ones of the above isocyanates respectively, and the like. Of the above organic polyisocyanates, MDI, crude MDI and their modified ones are particularly preferred.

30 The polytetramethylene ether glycol (hereinafter referred to as simply PTMEG) having a molecular weight of 400 to 2,000 used in the present invention is a diol obtained by the ring opening polymerization of tetrahydrofuran and is represented by the following general formula :

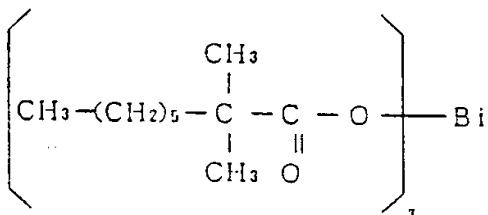


The organic polyisocyanate is mixed with the above polytetramethylene ether diol at a NCO/OH molar ratio of 5 to 40 and is reacted at about 80 °C for about 3 hours to obtain a partial prepolymer having NCO group at the molecular terminal.

40 Examples of the active aromatic polyamine used as the chain extender and free of the electron attractive group on the aromatic nucleus in the present invention include 4,4'-diaminodiphenyl, 4,4'-diaminodiphenyl ether, 2,3-, 3,4-, 2,4- and 2,6-diaminotoluene or mixtures thereof at various weight ratios, 2,4- and/or 4,4'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane, 1,3- and 1,4-phenylenediamine, naphthylene-1,5-diamine, polymethylene polyphenyl polyamine liquid polymer obtained by aniline-formaldehyde condensation, 1,3-dimethyl-2,4-diaminobenzene, 1,3-diethyl-2,4-diaminobenzene, 1,3-dimethyl-2,6-diaminobenzene, 1,4-diethyl-2,5-diaminobenzene, 1-methyl-3,5-diethyl-2,4-diaminobenzene (a), 1-methyl-3,5-diethyl-2,6-diaminobenzene (b), a mixture of (a) and (b) (hereinafter referred to as DETDA), 1,4-diisopropyl-2,5-diaminobenzene, 1,4-dibutyl-2,5-diaminobenzene, 2,4-diaminomesitylene, 1,3,5-triethyl-2,4-diaminobenzene, 1,3,5-triethyl-2,6-diaminobenzene, 1,3,5-triisopropyl-2,4-diaminobenzene and similar compounds; 2,3-dimethyl-1,4-diaminonaphthalene, 2,6-dimethyl-1,5-diaminonaphthalene, 2,6-diisopropyl-1,5-diaminonaphthalene, 2,6-dibutyl-1,5-diaminonaphthalene and similar compounds; 3,3',5,5'-tetramethylbenzidine, 3,3',5,5'-tetraisopropylbenzidine and similar compounds; 3,3',5,5'-tetramethyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane, 3,3',5,5'-tetrabutyl-4,4'-diaminodiphenylmethane, 3,5-diethyl-3-methyl-2,4-

diaminodiphenylmethane, 3,5-diisopropyl-3'-methyl-2,4-diaminodiphenylmethane, 3,3'-diethyl-2,2'-diaminodiphenylmethane, 3,3'-diethyl-4,4'-diaminodiphenylmethane and similar compounds; 3,3',5,5'-tetraethyl-4,4'-diaminodiphenyl ether, 3,3',5,5'-tetrakisopropyl-4,4'-diaminodiphenyl ether, and the like. The above aromatic polyamines are used alone or in combination and in an amount of preferably 30 to 160 parts ("parts" means "parts by weight" in the present invention) per 100 parts of polyol in the resin component.

The catalyst used in the present invention is a mixture containing an organobismuth compound as an effective ingredient and is prepared by reacting an organic carboxylic acid with a bismuth salt. Bismuth trineodecanoate (Trademark : COSCAT #83 by COSAN CHEMICAL CO., LTD.) is particularly preferred. This compound is represented by the following structural formula :



20

with about 57 % purity.

A partial prepolymer having a high NCO % and a high NCO/OH molar ratio is so highly active as to have high reactivity with water and to be easily able to foam. However, the use of the above catalyst not only promotes the reaction between isocyanato group and OH group, but also controls the reaction with moisture in the resin and air, resulting in that chain extending takes place at an early stage and the initial cheese-like appearance is not observed to exhibit rubber elasticity. As the result, the elastomer thus obtained has a high density. Moreover, the above catalyst is not decomposed at raised temperatures and has good heat resistance.

The catalyst is used in a amount of 0.2 to 2.0 % by weight based on the resin component.

30 The two components high pressure colliding and mixing spray machine is of such a type that the partial prepolymer component collides with the resin component under high pressure at a blow-off nozzle to be thoroughly mixed with each other and to be dashed and coated onto the application surface, for example, preferably including RIM Series, MODEL T-3 by GLAS-CRAFT, INC., MODEL-II by GUSMER Corp. and the like. These two components high pressure sprayers are such that the stock solutions are sprayed onto the 35 application surface under a blow-off pressure of 60 to 150 Kg/cm² and a mixture of the stock solutions forms fine particles, resulting in making it possible to obtain an even application surface and to obtain a fairly thick coating by one spraying.

Examples of the low molecular weight glycol preferably used in order to control reactivity on the 40 reaction for the preparation of the partial prepolymer in the present invention include dipropylene glycol, tripropylene glycol, tetrapropylene glycol, diethylene glycol, 1,3- and 2,3-butanediol, neopentylglycol and the like.

The above low molecular weight glycols are used alone or in combination, and in an amount of 1 to 20 % by weight based on polytetramethylene ether glycol with the result that the NCO/OH molar ratio between a mixture thereof with polytetramethylene ether glycol and the organic polyisocyanate is in the range of 45 from 5 to 40.

Partial prepolymer is made by a process, for example, as indicated in Rubber Age November, pp 46 ~ 47 (1973).

Other plasticizer and flame-retardant mixed with the resin component are as follows.

50 Examples of the above plasticizer include dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctyl adipate (DOA), tricresyl phosphate (TCP), chlorinated paraffin, and the like. The plasticizer is used in an amount of 2 to 20 % by weight, preferably 5 to 10 % by weight based on the resin component.

Examples of the flame-retardant include phosphoric acid esters such as tris-β-chloropropyl phosphate (FYROL PCF by AKZO JAPAN, Ltd.), tris-dichloropropyl phosphate (CRP marketed by DAIHACHI CHEMICALS, Co., Ltd.), tris-chloroethyl phosphate (CLP marketed by DAIHACHI CHEMICALS, Co., Ltd.) and the like ; bromine compounds such as dibromoneopentyl glycol, tribromoneopentyl alcohol and the like ; and the like.

The above flame-retardant is used in an amount of 2 to 30 % by weight, preferably 5 to 15 % by weight based on the resin component.

In the present invention, stabilizers, and if necessary organic or inorganic pigments or fillers are also used.

Examples of the stabilizer include positionally hindered phenols such as IRGANOX 1010 and 1076, trademark, marketed by CIBA GEIGY Co., Ltd., YOSHINOX BHT, BB and GSY-930, marketed by 5 YOSHITOMI SEIYAKU Co., Ltd., and the like ; bezotriazoles such as TINUVIN P, 327 and 328, marketed by CIBA GEIGY Co., Ltd. ; benzophenones such as TOMISOAP 800, marketed by YOSHITOMI SEIYAKU Co., Ltd., positionally hindered amines such as SANOL LS-770 and 744,TINUVIN 144, marketed by CIBA GEIGY Co., Ltd. ; and the like.

The stabilizer is used in an amount of 0.3 to 2 % by weight based on the resin component.

10 Examples of the above filler include glass fiber, carbon black, calcium carbonate, talc, kaolin, zeolite, diatomaceous earth, perlite, vermiculite, titanium dioxide and the like.

The filler is used in an amount of 5 to 10 % by weight based on the resin component.

A polytetramethylene ether glycol is used 70 to 90% by weight, and an active aromatic polyamine as a chain extender is used 10 to 30% by weight based on resin component.

15 In the practice of the present invention the partial prepolymer is taken as a component A, as it is or by preferably mixing therewith a proper amount of plasticizer in order to control a flow rate volumetric ratio between two components. On the other hand, a component B is formed by mixing polyol, the chain extender, the catalyst, the pigment and the like. The components A and B are blown off at a predetermined flow rate ratio from the two components high pressure spray machine to be sprayed onto the application 20 surface in a molar ratio (NCO/OH) of about 0.9 to 1.3, the spraying condition has desirably a temperature (usually 50 to 60 °C) wherein the viscosity of liquids (A) and (B) is desired to be under 200 cps, and the difference of pressure between both liquids to be normally under 14Kg/cm². In the case where the glass fiber is used as the filler, air is blown off as a chopped strand glass fiber is cut to length at a position of the head of a gun so that the glass fiber is mixed with both components while flying in the air. A mixture of the 25 components A and B, which has been applied onto a coated product, is cured within one to 10 seconds. As desired, the above procedure is repeated several times to obtain a coated product having a predetermined film thickness.

The spray urethane elastomer according to the present invention is used in lining or protective coating for iron structures such as pipe, tank and the like, waterproof materials such as concrete for the roof and 30 outside walls which need waterproofness, thick-coated protective coating for a thermal insulant such as rigid polyurethane foam, polystyrene foam, board or the like, seamless floor covering material, open mold molding by use of a mold made of metal or resin, and the like.

According to the present invention, spraying only of the stock solutions by use of the two components 35 high pressure spray machine accomplishes coating and the stock solutions are cured in one second to ten and several seconds after being sprayed without producing cells even when thick-coated. Therefore, the present invention makes it possible to effect wet-on-wet coating within a short period of time, resulting in making it possible to accomplish a coating having a predetermined thickness in a short period of time.

The present invention also makes it possible to accurately reproduce complicated configurations such as an uneven design on the surface of an object to be coated by a simple operation on the surface of the 40 object to be coated, because no cells are formed.

EXAMPLE

45 The present invention is explained more in detail by the following Examples.

The formulations in the following Examples and Comparative Examples are represented by g(gram).

(A) Preparation of partial prepolymer component (Isocyanate component) :

50 To a mixture of purified MDI (MDI-PH, marketed by MITSUI TOATSU CHEMICALS, INC.) and liquid MDI (MDI-LK, marketed by MITSUI TOATSU CHEMICALS, INC.) further including MDI(mixed) in Example 2 and MDI(mixed) only in Comparative Example 2, is added PTMEG, PPG or polyester polyol as shown in Table 1 to be reacted at 80 °C for 3 hours in a nitrogen atmosphere, followed by adding assistants such as flame-retardant and the like to obtain a partial prepolymer component (isocyanate component).

(B) Preparation of resin component :

The resin component is prepared by uniformly mixing the aforementioned PTMEG, PPG or polyester polyol, the aforementioned DETDA or 1,4-butanediol, the aforementioned COSCAT #83, toner, stabilizer and thelike according to the formulations shown in Table 1.

5

Examples 1 - 3

The formulations are as shown in Table 1.

10 The partial prepolymer component (solution A) and the resin component (solution B) are sprayed at a volumetric ratio of 1 : 1 to 1 : 2 by use of the following machine. The solutions are sent to a two components high pressure spray machine by a GRACO's supply pump (air-driven 2 : 1, 208-177 type) under an air pressure of 5 Kg/cm².

15 The spray machine used is a RIM Series marketed by GLAS-CRAFT INC., and is used under a pressure of about 140 Kg/cm² when stopped, and 105 to 119 Kg/cm² when sprayed. Temperature control of the solutions is carried out in such a manner that the heat exchanger in the body is set at 50 °C for solution A and 60 °C for solution B, and the electric current of the hose heater is 4 amperes. A flat chamber (No. 1) and tip (043-25) are mounted on a Probler gun marketed by GLAS-CTAFT, INC. to be used as a spray gun. Spraying is carried out 3 to 5 times by use of a 1 mm thick polypropylene sheet as a mold to obtain a sheet having a thickness of about 2 mm. Temperature and relative humidity under the spray conditions are 20 as shown in Table 1. The sheet thus obtained is cultured for 7 days in a thermostatic chamber at 23 °C, followed by being subjected to physical properties measurements according to JIS K-6301.

The physical properties of the sheet thus obtained are as shown in Table 2. The results of heat resistance test for the sheet obtained in Example 2 are as shown in Table 3.

25

30

35

40

45

50

55

Table 1
Formulation (g)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
(A) Partial prepolymer (isocyanate)									
MDI-PH	777	↔	287	↔	1,190	↔	775	667	687
MDI-LK	333	↔	143.5	↔	793	↔	333	333	172
MDI (Mixture)	—	↔	287	—	—	—	—	—	—
PTMEG-1,000	500	500	—	—	384	384	500	—	—
PTMEG-650	—	—	324.3	↔	—	—	—	—	—
DPG	—	—	—	—	15.5	↔	—	—	—
PPG-Diol-3000(OHV:37)	—	—	—	—	—	—	—	570	—
EA-2000 (OHV : 56.1)	—	—	—	—	—	—	—	—	250
FYROL®-PCF (flame-retardant) (AZZO JAPAN)	—	—	52.1	52.1	—	—	—	—	—
NCO(% by weight)	19	19	17	↔	24	↔	19	19	24
NCO/OH (mol ratio)	8.4	8.4	5.6	5.6	15	↔	8.4	20	26.5
Viscosity (CPS/25 °C)	700	700	1,000	1,000	400	400	700	350	600
Sp. Gravity	1.1	1.1	1.1	1.1	1.15	1.15	1.1	1.18	1.21

5
10
15
20
25
30
35
40
45
50
55

Table I (to be continued)

Formulation (g)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
(B) Resin									
PTMEG-1,000	66.6	←	—	—	—	—	66.6	—	—
PTMEG-1,500	—	—	—	—	75.8	←	—	—	—
PTMEG-650	—	—	79.2	←	—	—	—	—	—
DETDMA	28.4	←	15.3	←	18.7	←	28.4	—	—
PPG-Diol-2000(OHV-56)								73.2	—
EA-2000 (OHV)-56.1								—	67.5
1,4-BD								21.8	21.5
TINUVIN® #327(Stabilizer)								—	—
DOP								0.5	6.0
DHTDL(Catalysis)								—	—
COSCAT ® #83 (Catalyst)	0.5	—	0.5	—	0.5	—	1.0	1.0	0.5
Toner	4.5	4.0	5.0	4.5	5.0	4.5	—	—	0.5
IRGANOX® 1010(Stabilizer)	0.5	←	0.5	←	0.5	←	4.0	4.0	4.0
(CIBA GEIGY CO.)							0.5	—	0.5
NCO INDEX:[NCO/OH(molar ratio)]	1.1	←	1.05	←	1.05	←	1.1	1.1	1.1
(in curing)									
Formulation Ratio									
Volume (A)/(B)	1/1	←	1/1	←	1/2	←	1/1	1/1.5	1/2

Table 1 (concluded)

	Example 1	Comp. Ex. 1	Example 2	Comp. Ex. 2	Example 3	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
in molding Temperature (°C)	6.3 30	← ←	27.8 68	← ←	23 55	← ←	6.3 30	← ←	23 55
Relative humidity (RH) (%)									
Moldability									
Curability									

Note :

EA-2000
1,4-BDOHV
MDI-PHMDI-LK
MDI (mixture)

4,4'-Isomer + 2,4'-isomer (60/40 % by weight)

Polytetramethylene ether glycol. Mol. Weight: ca. 1,500

Polytetramethylene ether glycol. Mol. Weight: ca. 1,000

Polytetramethylene ether glycol. Mol. Weight: ca. 650

Dipropylene glycol

Mixture of 1-methyl-3,5-diethyl-2,4-diamino benzene and

1-methyl-3,5-diethyl-2,6-diaminobenzene (chain extender)

DETDI

Dibutyl tin dilaurate (catalyst)

DBTDL

Mixed and kneaded material of inorganic and/or organic pigment
and plasticizer

Table 2

	Physical property (thickness: ca. 2 mm)								
	Example 1	Comp. Ex.1	Example 2	Comp. Ex.2	Example 3	Comp. Ex.3	Comp. Ex.4	Comp. Ex.5	Comp. Ex.6
Density (g/cm ³)	0.99	0.86	0.98	0.80	0.99	0.76	Molded sheet develops into a	0.84	0.73
Hardness	59D	51D	97A	91A	93A	86A	shape like	85A	82A
M ₁₀₀ (Kg f/cm ²)	146	118	130	83	92	63	weakly	65	58
Tensile strength (Kg f/cm ²)	240	154	250	160	230	145	coagulated	95	80
Elongation (%)	260	170	290	200	340	270	cheese, disabling	380	240
Tear strength (Kg f/cm ²)	85	70	77	64	69	53	it to measure	45	42
							physical properties.		

Note :

Hardness (D: Shore-D, A: Shore-A)

M₁₀₀ 100% tensile modulus

Table 3

Heat resistance test (Maintenance of physical property %)					
(1) COSCAT #83 Catalyst (Sheet of Example 2)					
	Hardness	M ₁₀₀	Tensile strength	Elongation	Tear strength
Blank test	100	100	100	100	100
after 70 °C x 7 days	100	106	109	100	100
after 100 °C x 7 days	101	99	109	115	104
after 120 °C x 7 days	98	88	109	138	117
(2) DBTDL Catalyst (Sheet of Comparative Example 2)					
	Hardness	M ₁₀₀	Tensile strength	Elongation	Tear strength
Blank test	100	100	100	100	100
after 70 °C x 7 days	112	103	112	123	104
after 100 °C x 7 days	104	80	54	100	81
after 120 °C x 7 days	83	-	31	9	38

5

10

15

20

25

30

35

40

45

50

55

Comparative Examples 1-6

5 Physical properties of the sheets obtained by spraying solution (A) and solution (B) according to the formulations in Table 1 respectively under the same conditions as in Examples 1-3 by use of the same two components high pressure spray machine as in Examples 1-3, are as shown in Table 2. The results of heat resistance test for the sheet obtained in Comparative Example 2 are as shown in Table 3.

10 As shown in Table 1 to Table 3, the sheets obtained by use of COSCAT #83 catalyst according to the present invention have better physical properties, i.e. modulus, tensile strength, elongation and tear strength compared with those obtained by use of DBTDL catalyst.

The results of the heat resistance test show that the sheets obtained by use of COSCAT #83 catalyst have better physical properties compared with those obtained by use of DBTDL catalyst in all of the above 15 physical properties.

Even if COSCAT #83 is used, the use of low molecular weight glycol as the chain extender results in reducing the reaction rate to be unapplicable to the spray molding according to the present invention, in showing cheese-like appearance on curing and such undesirable appearance as to cause cracks etc.

20 **Claims**

1. A process for manufacturing a solventless spray urethane elastomer which comprises spraying directly onto a substrate, by use of a two components high pressure spray machine, in a NCO/OH molar ratio of about 0.9 to 1.3 of undermentioned (a) and (b) components.(a) a partial prepolymer component prepared by reacting an organic polyisocyanate and a polytetramethylene ether glycol having a molecular weight of 400 to 2,000 at a NCO/OH molar ratio of 5 to 40, and (b) a resin component prepared by mixing a polytetramethylene ether glycol, having a molecular weight of 400 to about 2000, an active aromatic polyamine as a chain extender and free of an electron attractive group on the aromatic nucleus and an 30 organobismuth compound as a catalyst.
2. A process as claimed in claim 1, wherein said polyisocyanate is a purified or crude diphenylmethane diisocyanate, or modified diphenylmethane diisocyanate.
3. A process as claimed in claim 1, wherein said chain extender is an aromatic polyamine hindered by being substituted by at least one alkyl group having 5 or less carbon atoms.
- 35 4. A process as claimed in claim 1, wherein said two components high pressure spray machine is of a colliding and mixing type.
5. A process as claimed in claim 1, wherein said organobismuth compound is bismuth trineodecanoate.
6. A process as claimed in claim 1, wherein a low molecular weight glycol is mixed therewith in the reaction for the preparation of the partial prepolymer.
- 40 7. A process as claimed in claim 1, wherein a plasticizer is mixed with the resin component.
8. A process as claimed in claim 1, wherein a flame-retardant is mixed with the resin component.
9. A process as claimed in claim 1, wherein a filler is used.

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89313583.0
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.)
Y, X	<u>WO - A1 - 87/07 287</u> (AMERON, INC.) * Claims; page 8, lines 11-35; page 9, lines 26-30; page 10, lines 6-8; page 11, line 19 - page 12, line 4 *	1-3, 5, 6, 9	C 08 G 18/10 C 08 G 18/50 B 05 D 1/02
Y	<u>WO - A1 - 86/06 387</u> (THERMOCELL DEVELOPMENT, LTD.) * Claims; page 6, lines 8-14; example 1 *	1, 3, 4 7-9	
A	<u>US - A - 4 267 299</u> (OECHSLE, III) * Claims; column 3, line 59 - column 4, line 2; column 5, lines 8-14 *	1-3, 6-9	
A	<u>EP - A1 - 0 093 861</u> (TEXACO DEVELOPMENT CORPORATION) * Claims; page 3, line 2 - page 4, line 19; page 6, lines 13-15 *	1-3	TECHNICAL FIELDS SEARCHED (Int Cl.) C 08 G 18/00 B 05 D
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
VIENNA	04-04-1990	WEIGERSTORFER	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

